KINETICS OF HYDRAZINIUM DIPERCHLORATE THERMAL DECOMPOSITION BY FLASH MASS THERMAL ANALYSIS*

J. A. Hammond, Yuji A. Tajima, W. Glenn Stapleton, W. E. Baumgartner

Lockheed Propulsion Company, Redlands, California

1. INTRODUCTION

The kinetic mechanisms of decomposition of propellant ingredients are of vital interest to the propellant chemist when it becomes necessary to forecast propellant thermal stability and shelflife, to determine the ignition and combustion kinetics of the propellant, and to predict the sensitivity of the propellant to impact (shock) or frictional forces. In each case, the energetics and mechanism of the initiation step, and the products formed thereby are important. These parameters are not easily obtained by most experimental techniques for measuring reaction kinetics.

2. BACKGROUND

Unique techniques for determining the energetics and kinetics of the initiating reaction which occur during pyrolysis of solid propellant ingredients have been developed. These techniques involve the use of very small samples coated on a platinum ribbon heater/thermometer mounted in close proximity to the electron beam of a Bendix Time-of-Flight (TOF) mass spectrometer. Heating of the sample by capacitor or battery discharge was synchronized with the TOF analysis cycles. These techniques afford several distinct advantages in the study of thermal decompositions:

- o The vacuum essential to operation of the TOF assures identification of the primary decomposition species.

- o A very small amount (5-10 micrograms) of sample is applied as a thin coating on a comparatively large mass of supporting ribbon, assuring close compliance of the sample temperature to the ribbon temperature at all times.

- o The inclusion of the platinum ribbon in a resistance bridge circuit so that it acts as its own thermometer to eliminate errors in temperature measurement associated with external measuring systems, i.e., emittance values for optical pyrometry, large heat sink and thermal lag of attached thermocouples or other heat-sensing devices.

- o Method sensitivity, resolution, wide response range, allows continuous separation and analysis of decomposition species at widely different reaction rates.

---

* This work was supported by Air Force Contract AF04(611)11385, from Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards, California, Air Force Systems Command, United States Air Force.

o The very rapid (3×10^7 °C/sec.) heating rate attainable with the capacitor discharge permits stepwise isothermal analysis of the sample decomposition at the desired pyrolysis temperature. This is essential for determining induction times to explosion, similar to Wenograd's method (Ref. 1). This method is called Isothermal Flash Mass Thermal Analysis (or Isothermal FMTA).

o The less rapid heating rates (10-1000°C/sec.) attainable over longer times (linear up to 2 sec. at 100°C/sec.) permit study of reactions which control the stability/shelflife of the material or propellants, as well as of the reactions which occur in the thermal wave zone at the surface of a burning propellant. All quantities measured by this system are mathematically differentials so that many factors may be derived without extensive, tedious, and possibly inapplicable calibration procedures. This method is called Dynamic FMTA.

o Reaction mechanisms can be inferred from the order of appearance and temperature of appearance of the various pyrolysis species.

These techniques were originated in 1962 for the study of the phenomena which occur in the fizz zone of a burning propellant when the temperature rises from that of the bulk of propellant ($\sim$300°K) to that of the flame (up to 3000°K), within a distance of approximately 1 millimeter, creating high temperature and concentration gradients. Subsequently, and with some modification, this technique has provided an equally powerful tool for elucidating the decomposition mechanisms and energetics of high energy binders and oxidizer pyrolyses at heating rates in the range of 100 to 200°C/sec. Data acquisition, as well as data reduction techniques, have been developed which are necessary to elucidate the detailed decomposition reactions for the primary products under a broad range of experimental conditions (e.g., heating rates). Mathematical models have been developed which have been used in conjunction with a computer to establish the temperature across the sample area on the platinum ribbon heater. A mathematical technique has been developed which takes advantage of the unique differential data acquisition mode during dynamic FMTA to derive reaction activation energies, and eventually, the absolute reaction rates.

3. EXPERIMENTAL TECHNIQUES

Thermal decomposition rates of propellants/propellant ingredients can be very high. The instruments and techniques used to study the pyrolysis of these compounds should, therefore, be capable of acquiring data at rates characteristic of the processes. The mass thermal analytical technique developed for such investigations utilizes the fast scan speed of the Bendix TOF mass spectrometer. The sample, weighing 5 to 20 micrograms, is coated on a resistive platinum ribbon which is located 2 millimeters from the ionizing electron beam of the mass spectrometer. The ribbon and sample is heated by means of a battery discharge for slow heating rates or a capicator discharge for fast heating rates. The ribbon forms one arm of a Wheatstone bridge, by means of which the temperature-time profile of the ribbon and sample is determined. For heating rates in the range of 10 to 1000°C/sec., the mass spectra displayed on an oscilloscope are monitored continuously by fast cinematography. The experimental arrangement is shown schematically in Figure 1.

a. The Bendix Time-of-Flight Mass Spectrometer (TOF)

The TOF instrument consists basically of three sections: the ionization chamber, the flight tube, and the detector multiplier. In the normal mode of operation, ions are produced by a beam of electrons of controlled energy every 50 to 100 microseconds. (A 100 microsecond cycle can be easily achieved). Immediately after the electron pulse, voltage pulses are applied which accelerate the positive ions with identical kinetic energies per unit charge into the flight tube. Because the flight tube is field-free, the ions travel at velocities proportional to $\sqrt{e/m}$ (e and m are charge and mass, respectively) and thus arrive at the detector at different times. The detector multiplies the signal resulting from each group of ions with given arrival times, yielding an intensity--arrival time (m/e) spectrum of the ions produced in the ionization chamber. When the voltage and electron pulses are applied every 100 microseconds, a complete spectrum (in the m/e range of interest here) is obtained every 100 microseconds.

Mass resolution of the Bendix is such that no more than a 1 percent peak height contribution exists between adjacent peaks (one mass unit apart) in the Hg spectrum at m/e of 200.

b. The Sample Holder

To achieve high heating rates, it is essential that the sample holder be of low mass (low heat content). Since it is desirable to electrically heat the sample, the geometry must be such as to ensure a reasonable electrical resistance for ohmic heating. The sample holder must also be constructed of a relatively non-reactive metal. All these constraints dictated the use of a platinum ribbon sample holder. The wide, flat ribbon (15 by 1.02 by 0.025 mm) permits distribution of the small sample over a large area, resulting in a very thin film which ensures good thermal contact and close compliance of sample temperature to the ribbon temperature.

A Bendix Direct Inlet Probe, Model 843A, which permits access to the mass spectrometer ionization chamber by means of a pumped vacuum lock, was adapted to support the platinum ribbon which bears the sample. The arrangement is shown in Figure 2. When the probe is positioned in the mass spectrometer, the sample is approximately 2 millimeters from the ionizing electron beam. This arrangement results in a higher intensity spectrum than would be possible for a system in which the sample was located at greater distances from the electron beam. Also, products which are shortlived may be detected before they decay to secondary species.

The ionization chamber is cryogenically pumped with two specially designed liquid nitrogen cold traps. Their function is two-fold; (a) the residual H_2O background is reduced to practically zero and (b) pyrolysis products which escape from the ionization region are trapped before they can rebound from the walls and reenter the ionization region. This insures that most of the products which are being analyzed are detected while in a high energy state and have not collided with sampling system walls.

c. Sample Heating System

In these experiments, the sample may be heated in two different modes: (a) flash heating (3×10^{7} °C/sec.) to an isothermal condition and (b) a slower temperature rate of increase which has been varied from 100-200°C/sec. In either case, the platinum filament constitutes one arm of a Wheatstone bridge. Just prior to each sample run, the bridge is nulled. As the ribbon is heated, its resistance changes and the bridge becomes unbalanced. The output signal of the bridge is fed to an oscilloscope and recorded photographically. The circuit diagram is presented in Figure 3.

The heating of the ribbon during Dynamic FMTA is produced by a 24-volt battery connected in series with the bridge. The rate of heating may be varied with a rheostat also in series with the bridge. This is the only method which was used for the work reported herein.

Flash heating of the sample to an isothermal condition for Isothermal FMTA is accomplished by discharging a high voltage from a capacitor through the platinum ribbon. The capacitor is charged by the hydrogen thyratron. A constant low voltage from a 24-volt battery serves as the bridge power supply which enables the temperature to be measured after the current surge from the capacitor has subsided. The duration of the capacitor discharge is less than 10 microseconds. As in the dynamic FMTA, the bridge output is fed to an oscilloscope and is recorded photographically.

In both modes, the resistance of the platinum ribbon is calculated from the well-known Wheatstone bridge relationships, using the bridge imbalance potential at selected time intervals. The temperature at each time is then derived from the known resistance-temperature behavior of the platinum ribbon.

d. Data Recording Techniques

Time-of-flight mass spectrometry lends itself well to fast pyrolysis studies because of its rapid sampling rate (10 KHz) over the spectrum of 12 to 250 mass units. This rapid rate permits the use of very small samples and small heat sources which characteristically possess low heat capacities and therefore require less energy for a given temperature increase.

Rapid analysis coupled with extremely short periods in which the pyrolysis products are available for detection present some stringent requirements for recording data. In these experiments, the time range of interest may be as short as a hundred microseconds or, at most, two seconds. Obviously, the data must be recorded photographically from an oscilloscope trace.

For the dynamic FMTA, a Milliken DBM-5C high speed framing camera was employed to photograph the spectrum oscilloscope trace at a speed of 200 frames/second or 1 frame each five milliseconds. In general, the nominal heating rate was 100°C/sec. With the small sample, the pyrolysis event was usually completed within two seconds. To synchronize the temperature trace oscilloscope with the spectrum displayed on the oscilloscope, a flashlamp was triggered simultaneously with the beginning of current input to the ribbon. The flash overexposes the first few frames

of the spectrum, thereby marking the beginning of the heating. The same trigger pulse that fires the flashlamp is also used to trigger the sweep of the temperature trace oscilloscope. Since the mass spectrograph operates continuously at 100 microsecond intervals, the experiment may be begun at any time without an error in time of greater than 100 microseconds. This presents no serious error in time or temperature for experiments lasting one second; covering 10,000 complete spectra. The mass spectra, from m/e = 12 to m/e = 250 are continuously displayed on another oscilloscope. This trace is photographed by a camera operating at 200 frames per second, so that data is recorded at five millisecond intervals. This is sufficiently fast to permit accurately following the species formed in reactions induced by heating at rates from 100 to 200°C/sec. In this heating rate range, the rate of temperature rise is 0.1 to 0.2°C/millisecond, which corresponds to 0.01 to 0.02°C/complete mass spectrum trace or to 0.5 to 1.0°C/frame of film. Therefore, errors in temperature correlation, induced by one or several frame uncertainty for the start of the experiment would introduce an error no greater than that involved in the initial (zero time) sample temperature measurement.

e. Sample Preparation

A critical step in this analysis technique is insuring that the sample is uniformly distributed over the surface of the pyrolyzing heat source. From the standpoint of heat transfer to the sample source heat capacity and low pressure requirement of the mass spectrometer vacuum the sample must be on the order of 5-20 micrograms to achieve the best results. Samples of solid oxidizers or fuels have been dissolved in suitable solvents and deposited on the center 0.5 centimeter of the platinum ribbon in a dry box. For example, HP_2 is applied to the surface as a uniform film of a known concentration in dry methyl alcohol by means of a micro syringe, and the solvent allowed to evaporate. The sample is then transferred, in a dry bag, to either the mass spectrometer or to a bell jar and subjected to vacuum for 2 to 20 hours to remove the last traces of solvent. The sample, on the ribbon and holder, is then affixed to a probe, inserted into position inside the mass spectrometer through the vacuum lock. The sample is then heated by the battery discharge for dynamic FMTA.

4. DATA REDUCTION AND ANALYSIS

a. Hydrazinium Diperchlorate (HP_2) Decomposition

The technique has been termed Dynamic Flash Mass Thermal Analysis (or Dynamic FMTA, for short). This terminology arises by anaology to thermal methods of analysis already in use, especially thermogravimetric analysis (TGA) techniques which it most closely resembles. There are two basic modes of operation. The first mode utilizes linearly programmed heating combined with continuous analysis by the mass spectrometer, and thus is analogus to dynamic TGA. The second mode uses an extremely fast heating to an isothermal condition, and thus resembles isothermal TGA. Since the heating rates in either mode are extremely rapid compared to those in common use, the heating mode is analogous to "flash" heating by other means. Therefore, the first and second modes are aptly described as Dynamic FMTA, and Isothermal FMTA, respectively. The dynamic FMTA method has been used to study the decomposition mechanisms and energetics of HP_2 and NC, and to establish the validity of the technique.

This method also closely resembles the Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC) techniques as regards linearly programmed sample heating rates and data evaluation, except that the data represent analytical time resolved mass spectra data instead of integrated caloric/thermal data, and a considerably faster instrument response time is provided by using high speed cinematography of the scope display rather than recorders (as in DTA).

The films taken of the mass spectral traces are analyzed frame-by-frame for the order of appearance of species, and the parent species deduced from structural considerations and comparison with standard mass spectra (when available). Figure 4 shows a typical sequence for HP_2.

It is expected that the key species in the initiation reaction(s) for thermal decomposition can be those which are attached to the molecule with the weakest bonds, and hence appear first (at low temperatures) in the films of the mass spectra. Several of the key species are selected, and their spectral intensities are plotted as a function of time (and/or temperature), as in Figure 5, to facilitate deduction of the pyrolysis mechanism. The data are consistent with the mechanisms postulated by Grelecki and Cruice (Ref. 2) and by Levy, Von Elbe, Friedman, Wallin and Adams (Ref. 3):

(1) $N_2 H_6 (ClO_4)_2$ (s) $\longrightarrow$ $N_2 H_5 ClO_4$ (s) + $HClO_4$ (g)

(2) $N_2 H_5 ClO_4$ (s) $\longrightarrow$ $N_2 H_4$ (g) + $HClO_4$ (g)

The first peak in the time/intensity plot is definitely due only to $HClO_4$, corresponding to equation (1), whereas the second peak has definite contributions from both N_2H_4 and $HClO_4$.

To be able to extrapolate the data obtained at one temperature and reaction rate to another temperature, e.g., shelflife prediction, combustion rates, etc., it is necessary to derive the activation energies and preexponential factors for the reactions. Fortunately, for the determination of the activation energy (E), absolute reaction rate data are not required, but only the shape of the curve and the slope which can be derived therefrom. In the uncalibrated mass spectrometer, the line intensity, I, of a given species is related to its partial pressure, P, in the ion chamber in an unknown but constant proportion during any particular experiment. P, in turn, is proportional to the difference between the rate of generation of a species and the rate at which it is removed by pumping and by injection into the flight tube as ions. The difference is also an unknown but constant factor during any given experiment.

Method I

If the rate of generation of a species can be represented by the Arrhenius rate expression as a first order reaction, then:

$$I \propto P \propto (1/x)(dx/dt) = k = A \exp.(-E/RT)$$

or

$$I = B \exp.(-E/RT)$$

Wherein B contains the Arrhenius frequency factor, A, the mass spectrometer system constants, and the fraction, x, of a given species which remains unreactive at any given time. Consideration of x as constant over a small time or temperature interval introduces only a small error in calculating E, since it is the fraction reacted which is important in this case, and not the absolute quantity. Taking the logarithm of the function yields:

$$2.303 \log I = -E/RT + 2.303 \log B$$

A plot of log I versus 1/T should yield a straight line with a slope of -E/(2.303R). The intercept at log I = 0 will yield a value of log B which may be of value later to evaluate A, specific reaction rates, and mass spectrometer system constants.

Method II

For complete definition of the reaction kinetics, the value of the reaction rate, reaction rate constant, or pre-exponential factor must be determined as well as the activation energy. The rate of disappearance of reactant, hence rate of appearance of products, during a first order reaction is given by:

$$dx/dt = kx$$

or:

$$(1/x)(dx/dt) = k$$

which is mathematically identical to:

$$d(\ln x)/dt = k \text{ (where } \underline{\ln} \text{ refers to natural logarithms)}$$

on integration between limits:

$$\ln x_2 - \ln x_1 = \ln (x_2/x_1 = k (t_2 - t_1)$$

Since the ratio x_2/x_1 is the same whether x is an absolute value or a fraction of the absolute value, the above rate expressions are likewise indifferent to the way in which x is expressed. This fact, together with the differential nature of the analytical technique provides the key whereby the absolute reaction rates and pre-exponential factors may be derived from the data taken by the uncalibrated system. The total area enclosed by the intensity/time curve for a given mass species represents the total quantity of that species which was formed as the result of the reaction. Any portion of the total area, taken at a definite time, then represents a definite fraction of the quantity of that species which has been formed. The total area, and suitable fractions thereof, taken at short time intervals during the initial stages of the reaction, can be replotted as ln x versus time. Since each time corresponds to a definite temperature, the slopes of the plot, taken at several times, correspond to values of the absolute reaction rate constant, k, taken at several temperatures. The ln k can then be plotted against reciprocal absolute temperature in the conventional manner, and both the activation energy and the pre-exponential factor, A, determined routinely.

It is expected that the activation energy for the thermal decomposition reaction of a compound will reflect the activation energy of the primary decomposition species. Therefore, the Arrhenius plots of the first detected species in the HP_2 decomposition calculated by Method I are presented in Figure 6. There are two distinct regimes - the first, "low temperature" regime (labeled "A" on the graphs) is driven solely by the energy input from the platinum ribbon, while the second, "high temperature" regime (labeled "B" on the graphs) is one in which autoacceleration of the reaction occurs.

Work on HP_2 was performed at Thiokol's Reaction Motors Division (RMD) (Ref. 2), using time-to-acceleration techniques with a closed vessel. This technique yields the activation energy for a reaction which occurs before autoacceleration - which corresponds to the "A" regime. The data as presented in Figure 6 for the "A" regime yields a value of 23 Kcal/mole, which compares remarkably well with the value of 23.5 Kcal/mole obtained at RMD. Thus, the validity of the experimental and data reduction techniques is established. The activation energy and frequency factor determined from the more detailed data treatment of Method II are given in Table I. It should be noted that the activation energy is determined from the first $\frac{1}{2}$% decomposition, and very small errors in the determination of the fractional areas will yield large errors in the value of the activation energy. Other large errors can be introduced when small errors are made in selecting the slopes from the curves of fraction reacted versus time (from which the reaction rate constant, k, is obtained). The slopes are very sensitive to the way in which the curves are drawn, and to personal judgment in estimating the tangent line. Under these circumstances, the agreement of the two sets of data is encouraging. Future determinations will be made with much more care over the first one to two percent of the decomposition in order to improve the accuracy of the results.

When the activation energy of 23 Kcal/mole is used with the absolute rate constants obtained in the detailed treatment, the Arrhenius factor is found to be $(5 \pm 2) \times 10^{13}$ sec.$^{-1}$, which is a reasonable value for these types of reactions.

It is of interest to note that the vacuum conditions prevailing in these experiments precludes the acceleration of the reaction by reaction products, so that another explanation for the observed acceleration must be sought. The experimental results show that the activation energy for the initial step changes from 23 Kcal per mole during the pre-acceleratory period to 86 Kcal per mole during acceleration. This means that the acceleration of the reaction (rate of change in reaction rate due to one degree centigrade temperature rise) is more than 12 times as great for the portion with the 86 Kcal/mole activation energy as for the portion with the 23 Kcal/mole activation energy.

b. Hydrazinium Monoperchlorate (HP) Sublimation

The postulated decomposition mechanism, chemical equations (1) and (2) suggests the possibility of also obtaining the heat of sublimation of HP from the FMTA data. Since N_2H_4 is characteristic of HP only, then the heat of sublimation should be found by applying the Clausius-Clapeyron equation to the m/e = 23 ion species ($N_2H_3^+$). The previous arguments regarding mass spectrometer system constants apply to this determination as well. The integrated form of the Clausius-Clapeyron equation is:

$$-\ln I \propto -\ln P = \left(\frac{\Delta H_{sub.}}{R}\right)\left(\frac{1}{T}\right) + \text{constant}$$

As before, the pressure ratios are equivalent to the intensity ratios, so that a plot of ln I versus 1/T will yield a straight line with slope equal to $-\Delta H_{sub.}/R$. From this plot, shown in Figure 7, the heat of sublimation, $\Delta H_{sub.}$, is calculated to be 32 Kcal/mole. This compares very well with the value of 29.2 Kcal/mole determined by Levy et alii (Ref. 3), using an equilibrium vacuum sublimation technique.

5. CONCLUSIONS

The FMTA technique has been shown to be a powerful tool for the investigation of thermal decomposition of solid materials since the reaction mechanisms and kinetic rate data can be obtained from a single experiment. In some cases, kinetic data (e.g., Arrhenius frequency factors) and primary decomposition species can be obtained by no other current technique. The results of the FMTA technique do not depend upon tedious, unreliable, and repeated mass spectrometric calibration procedures, therefore many more useful experiments can be performed with equipment previously considered unsuitable for quantitative measurements.

BIBLIOGRAPHY

1. J. Wenograd, "The Behavior of Explosives at Very High Temperatures", U.S. NOL, NAVWEPS Report 7328, Oct. 1960

2. C. J. Grelecki, W. Cruice, "Thermal Decomposition of Hydrazinium Monoperchlorate and Hydrazinium Diperchlorate", pp 73-81, in Advanced Propellant Chemistry, Advances in Chemistry Series 54, American Chemistry Society, Washington, D. C. (1966)

3. J. B. Levy, G. Von Elbe, R. Friedman, T. Wallin, S. J. Adams, "The Deflagration of Hydrazine Perchlorate", pp 55-72, ibid.

TABLE I

ENERGIES FOR HP_2 THERMAL EVENTS

Species	m/e	Decomposition Activation Energies (Kcal/mole) This Work A	B	(Ref. 2)
$HClO_4^+$ (parent)	100	23	86	23.5

HP HEAT OF SUBLIMATION (Kcal/mole)

Species	This Work	(Ref. 3)
$N_2H_3^+$ (from N_2H_4)	32	29.2

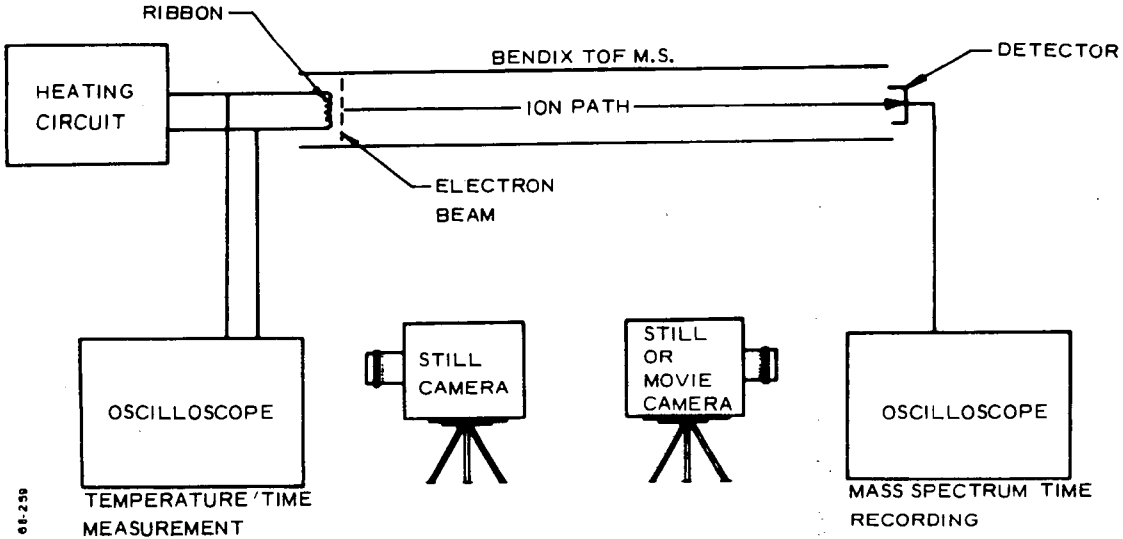

Figure 1 MTA Experiment Schematic

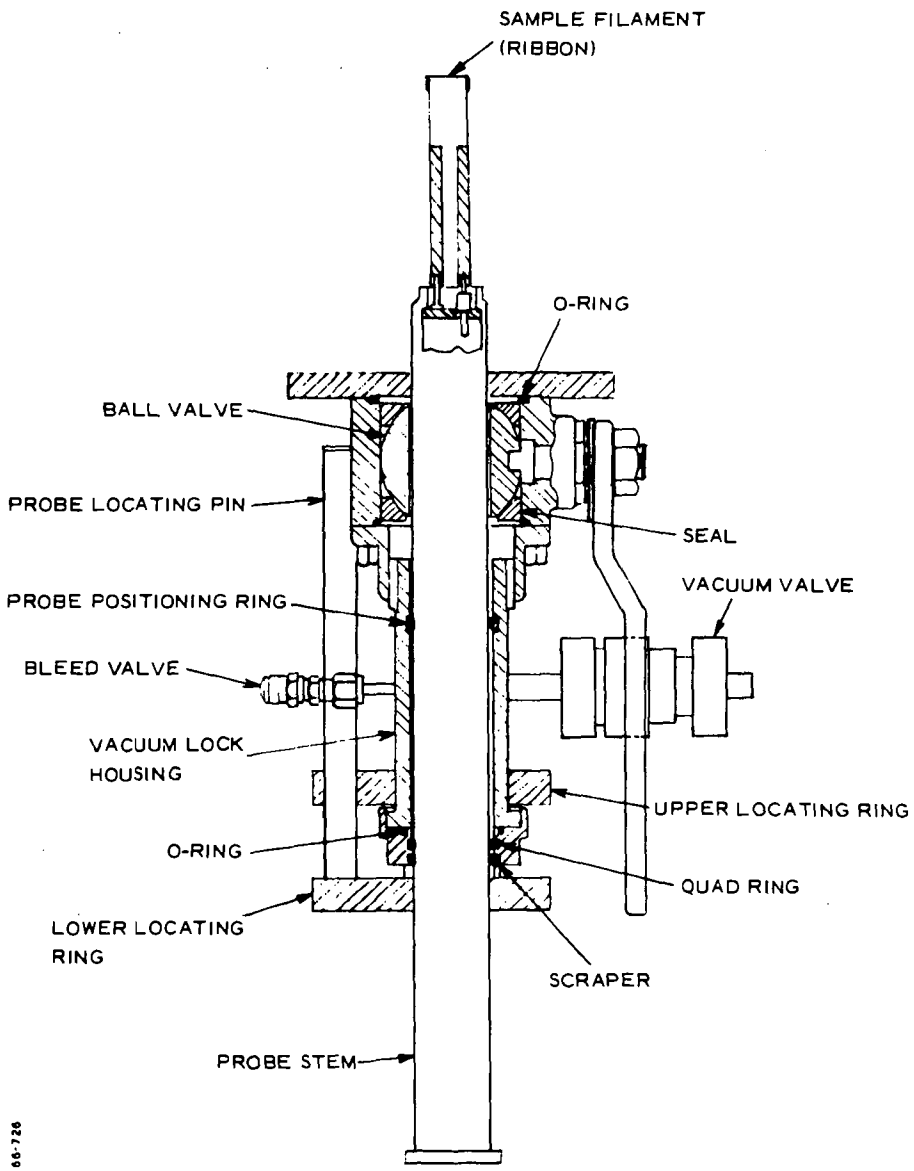

Figure 2 Bendix Direct Inlet Sample Probe

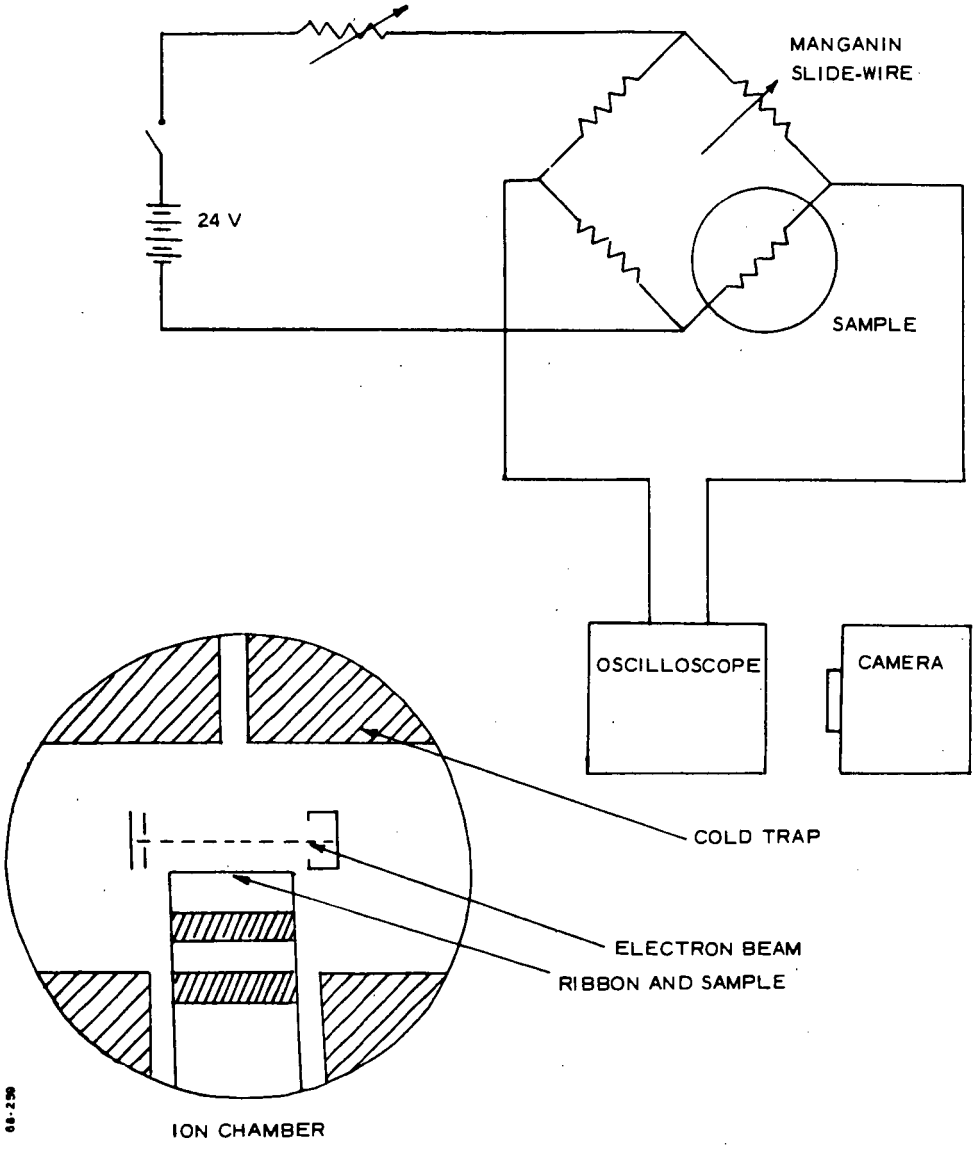

Figure 3 Dynamic FMTA Schematic

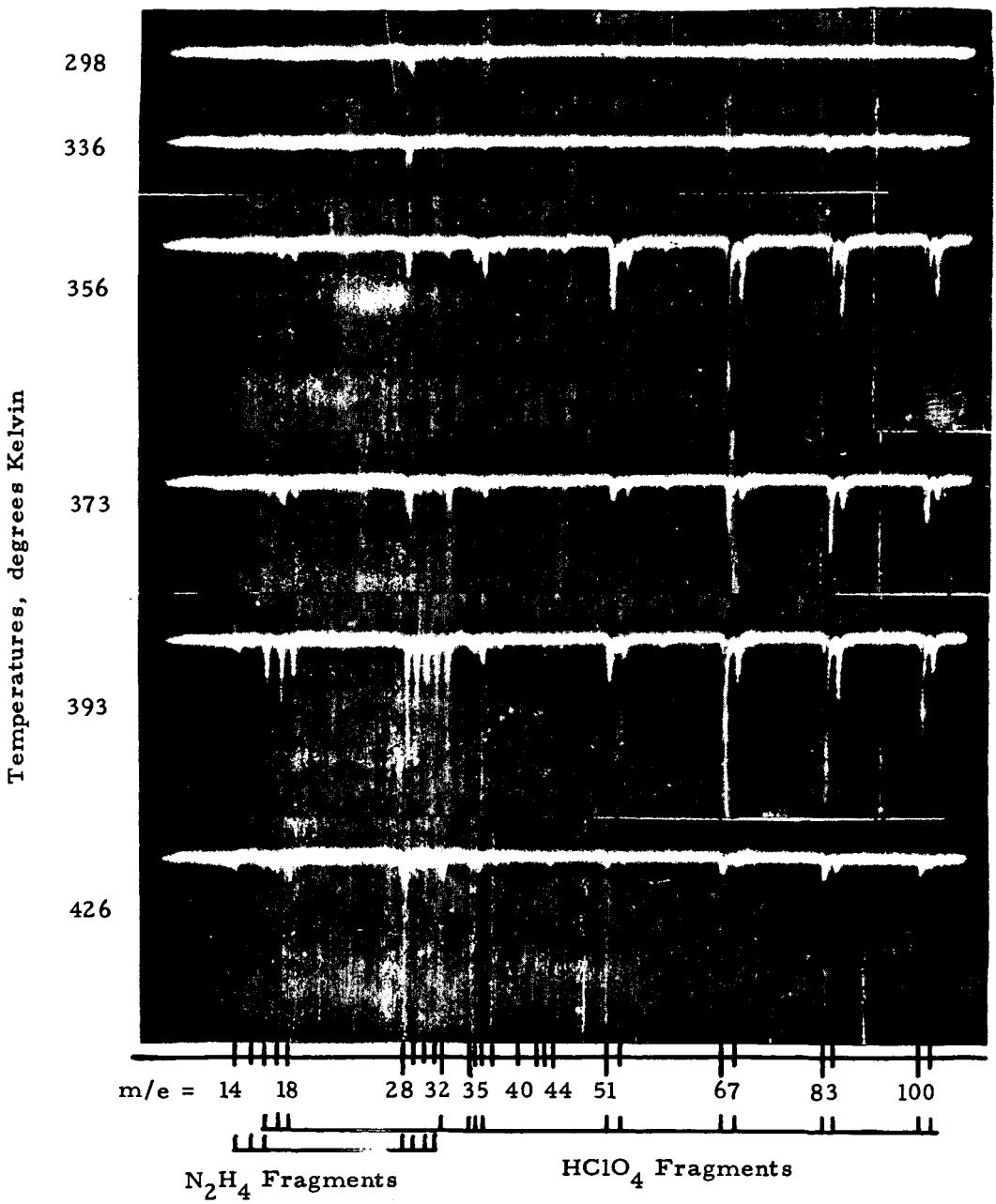

Figure 4 Mass Spectra from FMTA of HP_2

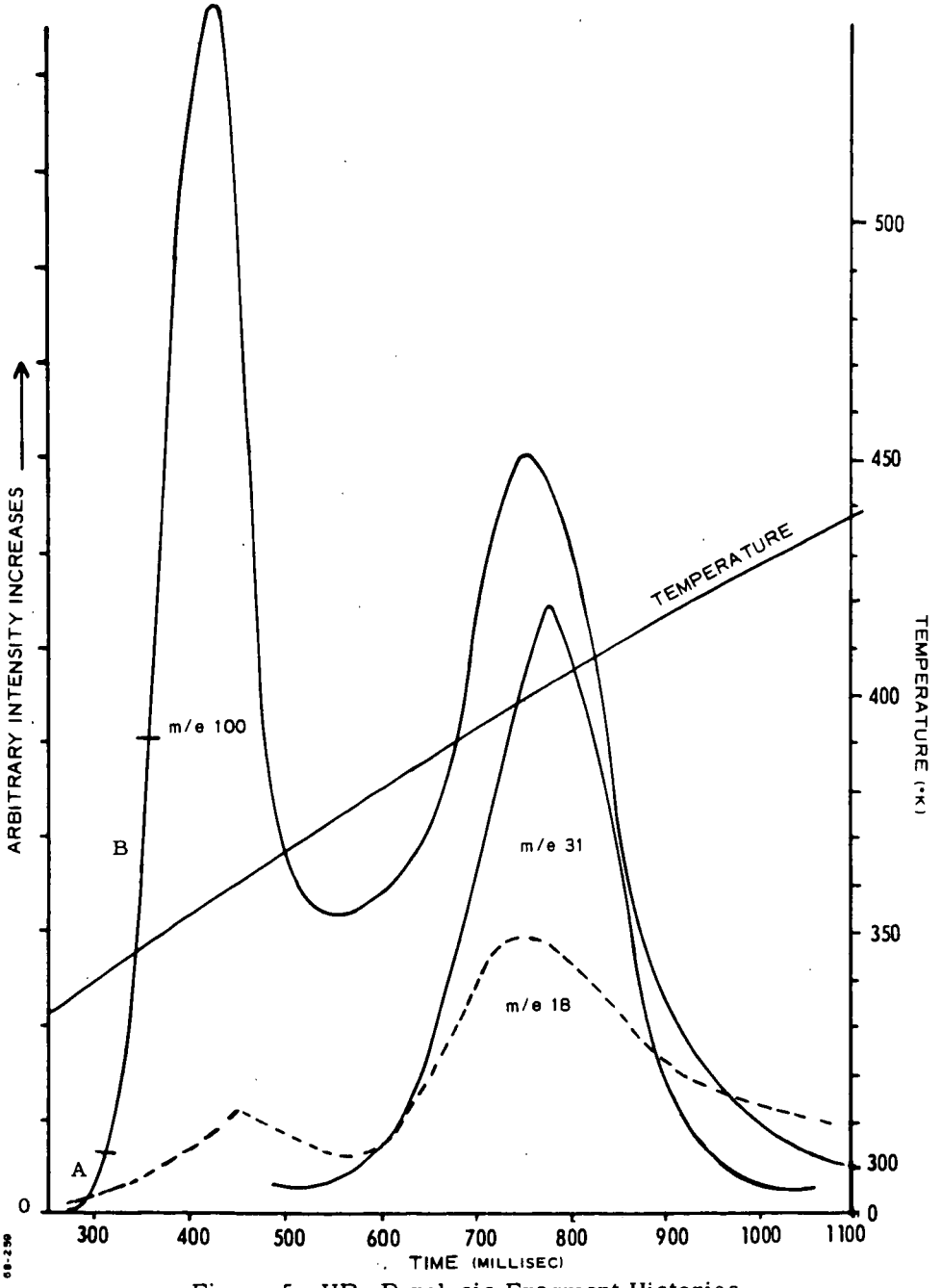

Figure 5 HP_2 Pyrolysis Fragment Histories

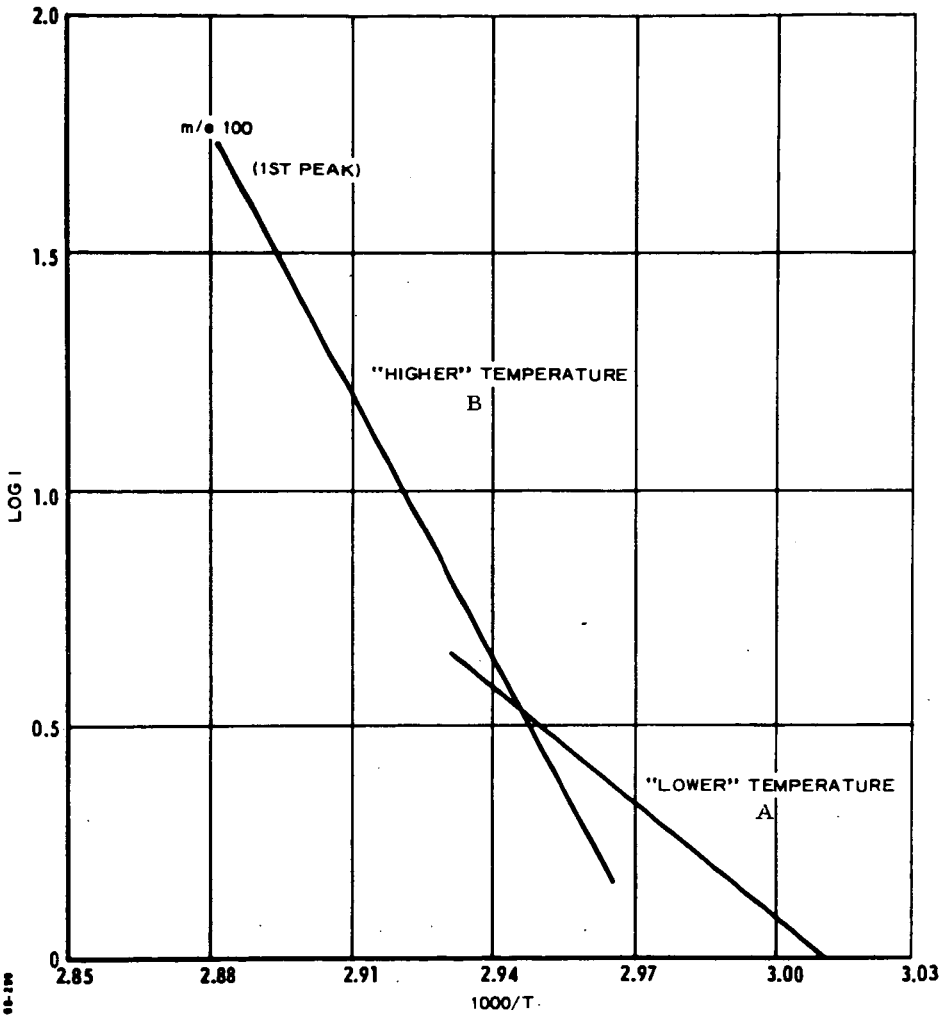

Figure 6 Arrhenius Plot of $HClO_4^+$ from Flash MTA of HP_2

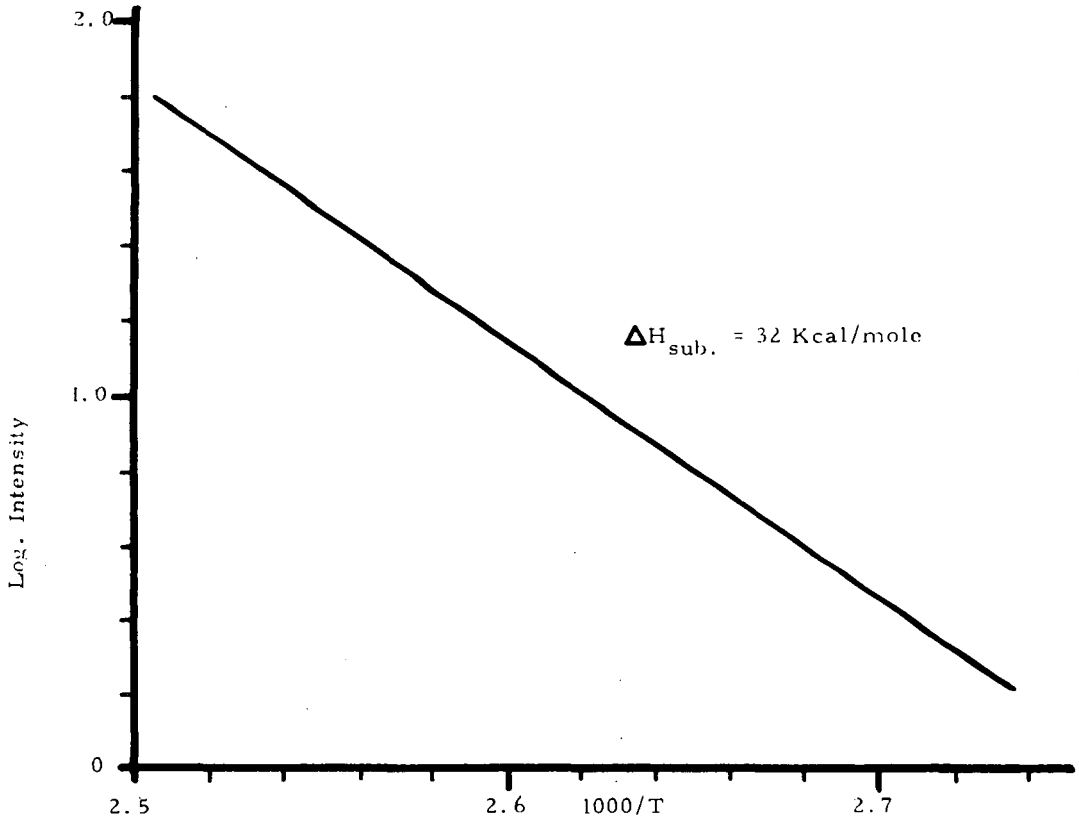

Figure 7 Clausius-Clapeyron Plot for HP Sublimation